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Abstract

Sodium ion batteries (SIBs) have been attracting much attention as promising next-generation energy storage devices for large-scale applications. The major safety issue with SIBs, which arises from the flammability and volatility of conventional organic solvent-based electrolytes, is resolved by adopting an ionic liquid (IL) electrolyte. However, there are only a few reports on the study of negative electrodes in ILs. Here, we report the electrochemical performance of a hard carbon (HC) negative electrode in Na[FSA]-[C_3C_1pyrr][FSA] (FSA = bis(fluorosulfonyl)amide, C_3C_1pyrr = N-methyl-N-propylpyrrolidinium) IL over a wide temperature range of −10 ºC to 90 ºC. High-temperature operation, which is realized for the first time by using an IL, can take full advantage of the high capacity of HC even at a very high discharge rate of 1000 mA $(g\text{-HC})^{-1}$: the discharge capacity is 230 mAh $(g\text{-HC})^{-1}$ at 90 ºC and 25 mAh $(g\text{-HC})^{-1}$ at 25 ºC. Moreover, surprisingly stable cycleability is observed for the HC electrode at 90 ºC, i.e. a capacity retention ratio of 84% after 500 cycles. Finally, a high full-cell voltage of 2.8 V and stable full-cell operation with Coulombic efficiency higher than 99% are achieved for the first time when using $NaCrO_2$ as the positive electrode at 90 ºC.

Keywords: Sodium secondary battery; Hard carbon negative electrode; Ionic liquid; Wide temperature range; Full-cell performance

1. Introduction

Lithium ion batteries (LIBs) have been extensively researched and applied in the field of portable electronics, e.g. in mobile phones, cameras, and notebook computers, because of their high energy and power density.[1-4] LIBs have been also attracting interest for applications in electric vehicle systems and household storage cells, where there is a need for superior performance and large battery size. However, from the viewpoint of resource strategy, LIBs are unsuitable for use in large-scale electrical energy storage because of their relatively high cost and the uneven distribution of lithium sources. Sodium, on the other hand, is relatively less expensive and more abundant (sodium can be easily obtained from seawater or the earth's crust). Therefore, sodium ion batteries (SIBs) are considered promising alternatives to LIBs for large-scale energy storage.

Graphite has been widely used as the negative electrode in LIBs because of its high energy density and low cost. However, when used as the negative electrode in SIBs, graphite is electrochemically inactive, and only a limited number of sodium ions can be intercalated into graphite.[5] In recent years, many materials, including carbonaceous materials,[6-15] as well as $Na_2Ti_3O_7$,[16-20] $Na_4Ti_5O_{12}$,[21] TiO_2,[22-24] SnO_2,[25, 26] and alloys,[27-31] have been developed for use as negative electrode materials for SIBs. Among them, carbonaceous materials have attracted

much attention because of their relatively high capacity, natural abundance, safety, and nontoxicity. Alcantara et al. investigated the performance of carbon black as the negative electrode material for SIBs, and obtained a reversible capacity of 200 mAh g^{-1}.[6] Alcantara et al. also used carbon microparticles as the negative electrode material and showed a maximum reversible capacity of 285 mAh g^{-1}.[7] Cao et al. reported that hollow carbon nanowires showed a reversible capacity of 251 mAh g^{-1} and 82% capacity retention over 400 cycles at a current density of 50 mA g^{-1}.[8] Tang et al. demonstrated that hollow carbon nanospheres possessed excellent cycling stability and rate capability, and showed a reversible capacity of 223 mAh g^{-1} at 50 mA g^{-1}.[9] Recently, much attention has been paid to hard carbon (HC) because of its relatively high capacity. Komaba et al. investigated the electrochemical insertion of Na into HC, and demonstrated reversible capacities of 220–250 mAh g^{-1} in different organic electrolytes at 25 mA g^{-1}.[10] Zhao et al. reported a reversible capacity of 321 mAh g^{-1} for an HC electrode at a current density of 20 mA g^{-1}.[11] Ponrouch et al. synthesized HC by sugar pyrolysis and demonstrated that this material had a reversible capacity of >300 mA g^{-1}.[12] Hong et al. synthesized HC from biomass and found that porous HC exhibited a reversible capacity of 315 mA g^{-1} at 50 mA g^{-1}.[13]

All the above studies were conducted in organic solvent-based electrolytes such as $NaClO_4$/propylene carbonate or ethylene carbonate solution, which are highly volatile

and flammable and are hence unsuitable for use in the construction of large-scale safe batteries. Ionic liquids, which are generally non-flammable and have negligibly low volatility as well as high thermal and electrochemical stability, have been considered as safer electrolytes for SIBs when compared with the organic solvent-based electrolytes. Na[TFSA]-Cs[TFSA] (TFSA = bis(trifluoromethylsulfonyl)amide), Na[FSA]-K[FSA] (FSA = bis(fluorosulfonyl)amide), and Na[FSA]-[C_3C_1pyrr][FSA] (C_3C_1pyrr = *N*-methyl-*N*-propylpyrrolidinium) ionic liquids have been reported as suitable electrolytes for sodium secondary batteries.[32-35] Among them, Na[FSA]-[C_3C_1pyrrr][FSA] ionic liquids can be operated in a wide temperature range and show better electrochemical performance.[34,35] In our previous study, we investigated the electrochemical performance of HC electrodes in Na[FSA]-K[FSA], Na[FSA]-[C_3C_1pyrr][FSA] and Na[FSA]-K[FSA]-[C_3C_1pyrr][FSA] ionic liquids at 90 ºC.[36] We found that ionic liquids containing K^+ ions, such as Na[FSA]-K[FSA] and Na[FSA]-K[FSA]-[C_3C_1pyrr][FSA], are not suitable for the use of HC electrodes because of the irreversible K^+ ion insertion into HC. On the other hand, the Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid was found to be suitable for the use of HC electrodes exhibiting a reversible capacity of 260 mAh g^{-1} at 90 ºC.[36] However, there is no report on the temperature dependence of the electrochemical performance of the HC electrode in the Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid. We have also

investigated the viscosity and ionic conductivity of the Na[FSA]-[C_3C_1pyrr][FSA] ionic liquids at different temperatures, and reported the effect of operation temperature on the electrochemical performance of $NaCrO_2$ positive electrodes.[37] In the similar manner, it is worth investigating for the HC electrodes the role of high-temperature operation on improvement of the electrode performance as compared that observed during conventional room temperature operation. Therefore, in this study, the electrochemical performance of an HC electrode in Na[FSA]-[C_3C_1pyrrr][FSA] ionic liquid was investigated over a wide temperature range between −10 ºC and 90 ºC. Moreover, to demonstrate the practical applicability of HC electrode, a full cell was fabricated using $NaCrO_2$ as the positive electrode, and its performance was investigated for the first time at 90 ºC.

2. Experimental

2.1 Materials

Commercially available HC powders (Carbotron P S(F), Kureha Battery Materials Japan Co., Ltd.) were used without any purification or treatment. Na[FSA] (Mitsubishi Materials Electronic Chemicals Co., Ltd., Japan, >99.0%) and [C_3C_1pyrr][FSA] (Kanto Chemical Co., Inc. Japan, >99.0%) were dried under vacuum at 60 ºC for 24 h. Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid electrolyte was prepared by mixing Na[FSA] and [C_3C_1pyrr][FSA] in 2:8 molar ratio. Reagent-grade acetylene black (AB; Wako Pure Chemical Industries),

polytetrafluoroethylene (PTFE; Sigma-Aldrich), *N*-methyl-2-pyrrolidone (NMP), polyamide-imide (PAI; SOXR-O, 18.96 wt% NMP solution, Nippon Kodoshi Corporation, Japan) binder, and metallic sodium were used. $NaCrO_2$ powders were synthesized by mixing Na_2CO_3 and Cr_2O_3 and baking the mixture at 850 ºC for 5 h under Ar flow.

2.2 Electrochemical characterization

The HC electrodes were fabricated by a conventional coating method. A slurry consisting of HC (96 wt%) and PAI (4 wt%) in NMP was uniformly coated onto Al foil. The HC electrodes were dried in a vacuum line at 200 ºC overnight before being transferred into an Ar-filled glove box. For preparation of the positive electrode, the $NaCrO_2$ powders were mixed thoroughly with AB and PTFE in a weight ratio of 80:15:5, using a mortar and pestle. The obtained mixture was pressed onto an aluminium mesh at 300 MPa. Electrochemical characterization was performed using 2032 type coin cells. Half-cells were fabricated with HC for the working electrode and sodium foil for the counter electrode. A full cell with HC and $NaCrO_2$ electrodes was also fabricated using a 2032-type coin cell. A glass fiber filter (Whatman, GF-A, 260 mm) was used as a separator. The electrodes and separators were vacuum-impregnated with Na[FSA]-[C_3C_1pyrr][FSA] at 60 ºC before assembling the cells. These cells were assembled in an Ar-filled glove box (dew point < −80 ºC). Charge-discharge tests were conducted at constant current rates of 20–2000 mA (g-HC) $^{-1}$ over the voltage range 0.005–1.5 V and temperature range −10 to 90 ºC. Electrochemical impedance measurements of the Na/HC, Na/Na, and

HC/HC cells were performed in the frequency range of 500 kHz to 100 mHz with an AC voltage signal of 10 mV.

3. Results and discussion

The charge-discharge curves of the HC electrode measured at 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$ are shown in Fig. 1. In the first cycle, a plateau is seen in the voltage range of 1.2-1.4 V during the charge process. The plateau at about 0.1 V in the charge-discharge curves corresponds to the insertion/ extraction of Na ions into/from HC. In the first cycle, the HC electrode exhibits a charge capacity of 353 mAh $(g\text{-}HC)^{-1}$ and a discharge capacity of 277 mAh $(g\text{-}HC)^{-1}$, showing 78.5% initial Coulombic efficiency. The irreversible capacity in the first cycle would be attributed to the formation of solid electrolyte interphase (SEI) on the surface of the HC electrode. In the subsequent cycles, the HC electrode shows a reversible discharge capacity of about 274 mAh $(g\text{-}HC)^{-1}$.

To investigate the effect of operation temperature, charge-discharge tests were performed for the Na/HC half-cell at −10 to 90 ºC. Fig. 2 shows the charge-discharge curves at a current rate of 20 mA $(g\text{-}HC)^{-1}$. The HC electrode exhibits a discharge capacity of 193 mAh $(g\text{-}HC)^{-1}$ at 25 ºC, corresponding to about 70% of the initial discharge capacity at 90 ºC. At temperatures above 25 ºC, the shapes of the charge-discharge curves are similar, and a plateau appears at voltages below 0.2 V.

However, the plateau disappears at temperatures below 25 ºC. Naturally, the capacity decreases largely below 25 ºC. The discharge capacities are 48 and 10 mAh $(g\text{-HC})^{-1}$ at 0 and −10 ºC, respectively.

The lower capacity of the Na/HC half-cell at low temperatures indicates the high internal resistance. The possible reasons for this are the reduced ionic conductivity, limited diffusivity of sodium ions in HC, and increased charge-transfer resistance at either the HC or sodium metal. For a better understanding of the effect of operation temperature on capacity, electrochemical impedance measurements were carried out for the Na/HC, Na/Na, and HC/HC cells at 0-90 ºC. Fig. 3a shows the impedance spectra of the Na/HC cell at 0-90 ºC. It can be seen that the resistance of the Na/HC cell increases with decreasing temperature, especially at temperatures below 25 ºC. The high-frequency limit is the electrolyte resistance (Re). The semicircle at the middle frequency corresponds to the charge-transfer process at the electrode/electrolyte interface. Since the charge-transfer resistance (Rct) is much larger than Re, the cell resistance mainly results from Rct. The Rct value increases with decreasing operation temperature, indicating significant sensitivity to temperature. Figs. 3b and 3c show the impedance spectra of the Na/Na and HC/HC symmetric cells at different temperatures. The Rct value for the Na electrode is much larger than that for the HC electrode; further, Rct for the Na electrode increases quickly at temperatures below 0 ºC. This

indicates that the major component of *R*ct in the Na/HC cell originates from the Na counter electrode, especially at lower temperatures.

Fig. 4 shows the rate performance of the HC electrode at 25-90 ºC. The charge-discharge curves at 90 ºC for different current rates of 20-2000 mA $(g\text{-}HC)^{-1}$ are shown in Fig. 4a. With an increase in the current rate, the general shape of the charge-discharge curves remains unchanged, and all the curves have a plateau at voltages below 0.2 V. However, the capacity decreases gradually with an increase in the current rate. Fig. 4b shows the rate capability of the HC electrode at 90 ºC. The discharge capacity at a current rate of 200 mA $(g\text{-}HC)^{-1}$ is 261 mAh $(g\text{-}HC)^{-1}$, which is about 94% of the initial capacity at 20 mA $(g\text{-}HC)^{-1}$. Surprisingly, at a very high current rate of 1000 mA $(g\text{-}HC)^{-1}$, the discharge capacity is maintained at 230 mAh $(g\text{-}HC)^{-1}$, corresponding to about 82% of the initial capacity. For HC electrodes operated in organic solvent-based electrolytes at room temperature, the capacity retention ratio is less than 50% at high current rate of large than 500 mA g^{-1}.[13] The high capacity retention ratio in the present study is attributed to the high Na^+ ion conductivity of Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid at 90 ºC.[35] Except for the initial few cycles, the Coulombic efficiencies are higher than 99%. After cycling at high currents, the discharge capacity recovers to the original value at a low current rate, indicating good tolerance for the rapid Na ion insertion and extraction. Fig 4c

compares the rate capabilities of the HC electrode at 25, 50, and 90 ºC. The results clearly show that the HC electrode exhibits better high-rate capability at high operation temperatures. At low operation temperatures, the C/C_0 ratio (C: discharge capacity at a given current rate; C_0: discharge capacity at a current rate of 20 mA g^{-1}) decreases quickly with an increase in the current rate. At 25 ºC, the capacity retention is about 63% and 23% for current rates of 50 and 200 mA $(g\text{-HC})^{-1}$, respectively. At high temperature of 90 ºC, the ionic liquid has a high conductivity and the cell shows a low charge-transfer resistance. In contrast, the conductivity is low and the charge-transfer resistance is high at low temperature of 25 ºC, which limits the rapid insertion/de-insertion of sodium. Thus, the HC electrode has better high-rate capability at high operation temperatures.

Fig. 5 shows the cycling performance of the HC electrode with a constant current rate of 200 mA $(g\text{-HC})^{-1}$ at 25 and 90 ºC. At 90 ºC, the discharge capacity decreases gradually, and a reversible capacity of 229 mAh $(g\text{-HC})^{-1}$ is retained after 500 cycles, corresponding to a capacity retention ratio of 84%. Except for the initial few cycles, the Coulombic efficiencies are higher than 99%. At 25 ºC, the discharge capacity increases gradually before 100 cycles and then remains almost constant until 500 cycles. The Coulombic efficiencies are also higher than 99% except for the initial few cycles. This indicates that the HC electrode is stably operated at 25-90 ºC.

Finally, the charge-discharge performance of a coin-type full SIB using HC as the negative electrode and $NaCrO_2$ as the positive electrode is investigated at 90 ºC. A Na/$NaCrO_2$ half-cell has been shown to exhibit a high reversible capacity of about 120 mAh $(g\text{-}NaCrO_2)^{-1}$ between 2.5 and 3.5 V at 90 ºC.[37] Fig. 6 shows the charge-discharge curves of an HC/$NaCrO_2$ full cell between 1.5 and 3.5 V at 90 ºC. Several voltage plateaus are distinguishable in the charge-discharge curves, which are ascribed to the phase transitions of the $NaCrO_2$ electrode.[38, 39] The HC/$NaCrO_2$ full cell exhibits a charge capacity of 326 mAh $(g\text{-}HC)^{-1}$ and a discharge capacity of 263 mAh $(g\text{-}HC)^{-1}$ in the first cycle. The irreversible capacity in the first cycle can be attributed to SEI formation on the surface of the HC electrode, as discussed above. In the subsequent cycle, the full cell shows a reversible discharge capacity of about 260 mAh $(g\text{-}HC)^{-1}$ with a Coulombic efficiency of more than 99%. The discharge capacity of the HC/$NaCrO_2$ full cell is higher than that of the HC/$NaNi_{0.5}Mn_{0.5}O_2$ full cell using organic solvent-based electrolyte,[10] indicating that the HC electrode shows better electrochemical performance in the Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid electrolyte. This is due to the high Na+ ion conductivity of Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid at high temperature.[35] Since the HC electrode exhibited good cyclability with a capacity retention of 84% after 500 cycles, as shown in Fig.5, the full cell is well expected to have good cyclability. We are now investigating the performances, e.g.,

energy density, power density and cyclability, for several types of full cells at 25-90 ºC, which will be reported in the near future.

4. Conclusions

The electrochemical performance of an HC electrode in Na[FSA]-[C_3C_1pyrr][FSA] ionic liquid has been investigated in detail over the temperature range -10 to 90 ºC. The operation temperature strongly affects the electrochemical performance of the HC electrode. The HC electrode shows a reversible discharge capacity of 274 mAh $(g\text{-HC})^{-1}$ at 90 ºC, which decreases rapidly to 48 mAh $(g\text{-HC})^{-1}$ at 0 ºC. This result implies that the HC electrode is more suitable for operating at high temperatures. The HC electrode shows better rate capability at high operation temperatures. An HC/$NaCrO_2$ full cell shows a high reversible discharge capacity of about 260 mAh $(g\text{-HC})^{-1}$ at 90 ºC, which indicates that the HC electrode is a promising, safe negative electrode for ionic liquid-based SIBs.

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Figure Captions

Figure 1: Charge-discharge curves of the HC electrode at 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.

Figure 2: Charge-discharge curves of the HC electrode at -10 to 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.

Figure 3: Impedance spectra of the (a) Na/HC, (b) Na/Na, and (c) HC/HC cells at 0-90 ºC.

Figure 4: (a) Charge-discharge curves and (b) rate capability of the HC electrode at 90 ºC with current rate of 20-2000 mA $(g\text{-}HC)^{-1}$; (c) Comparison of rate capability of the HC electrode at 25, 50 and 90 ºC.

Figure 5: Cycling performance of the HC electrode at 25 and 90 ºC. Current rate: 200 mA $(g\text{-}HC)^{-1}$.

Figure 6: Charge-discharge curves of the HC/$NaCrO_2$ full cell at 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.

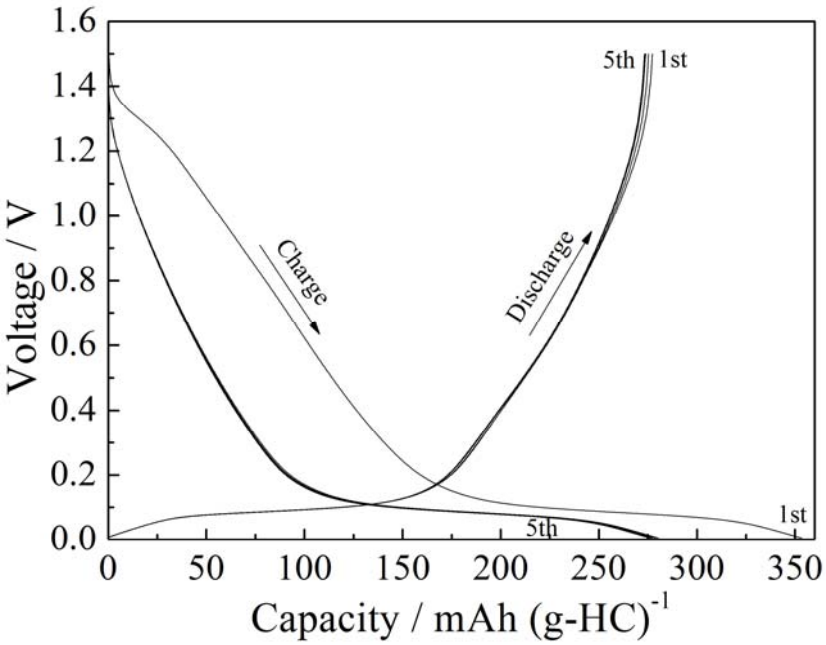

Fig. 1 Charge-discharge curves of the HC electrode at 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.

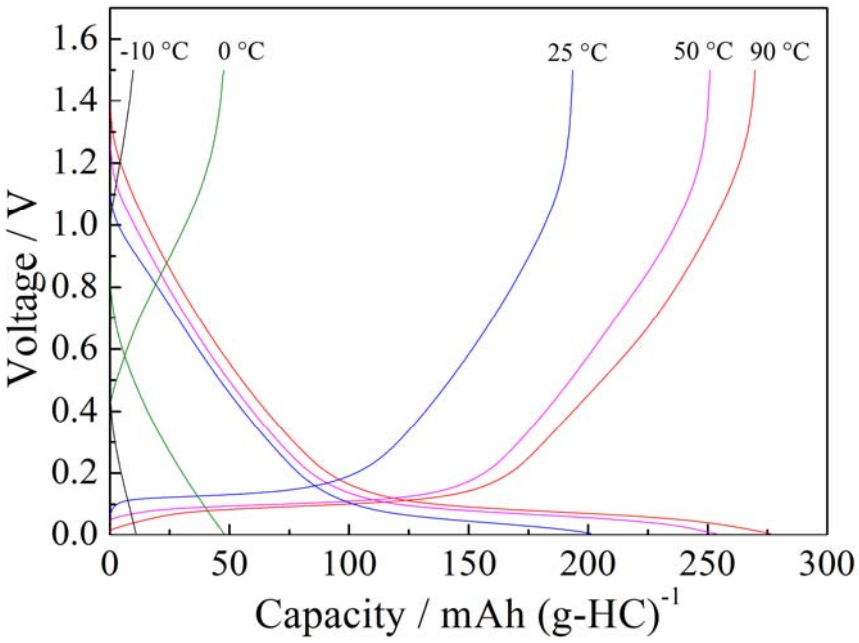

Fig. 2 Charge-discharge curves of the HC electrode at -10 to 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.

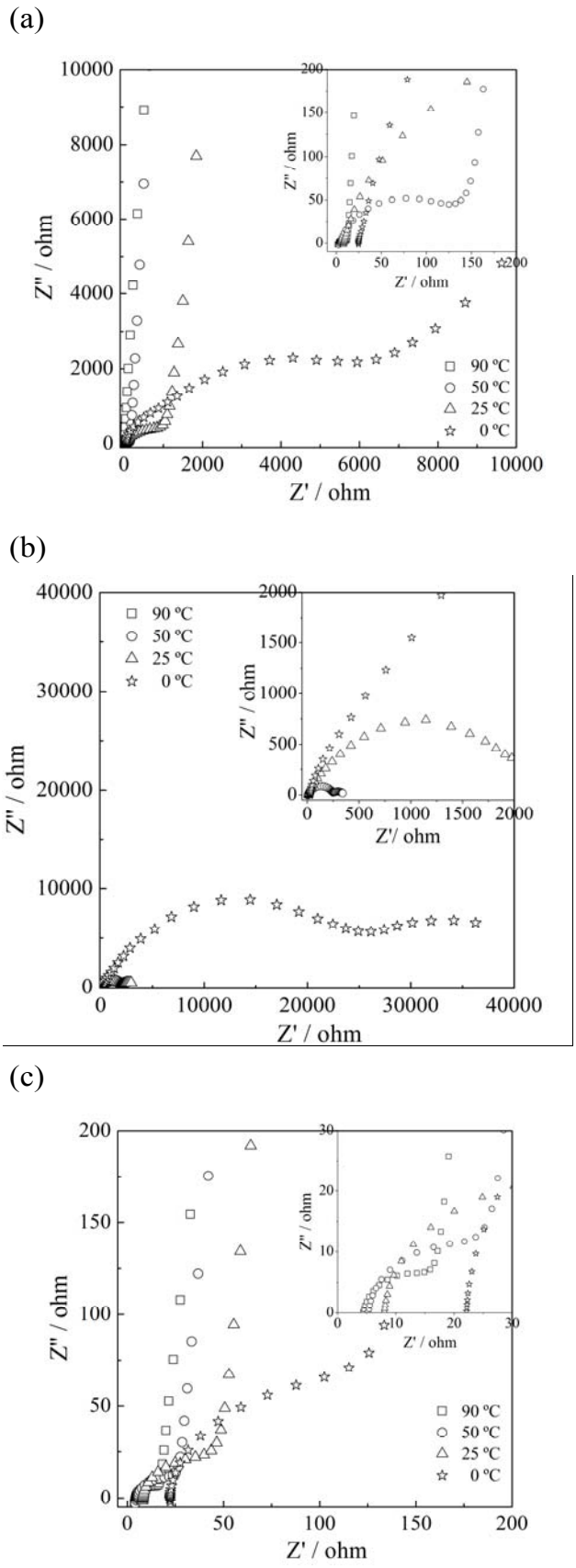

Fig. 3 Impedance spectra of the (a) Na/HC, (b) Na/Na, and (c) HC/HC cells at 0-90 ºC.

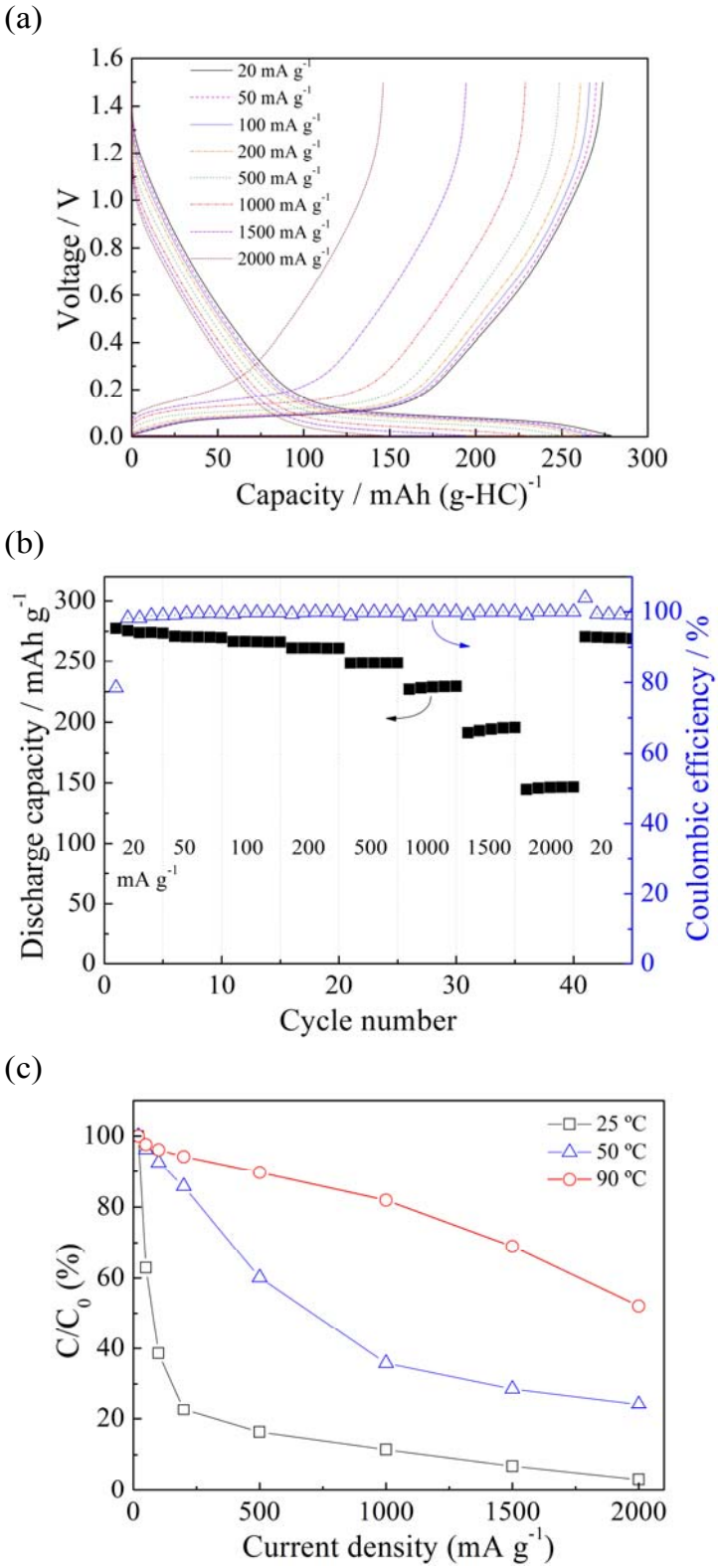

Fig. 4 (a) Charge-discharge curves and (b) rate capability of the HC electrode at 90 ºC with current rate of 20-2000 mA $(g\text{-}HC)^{-1}$; (c) Comparison of rate capability of the HC electrode at 25, 50 and 90 ºC.

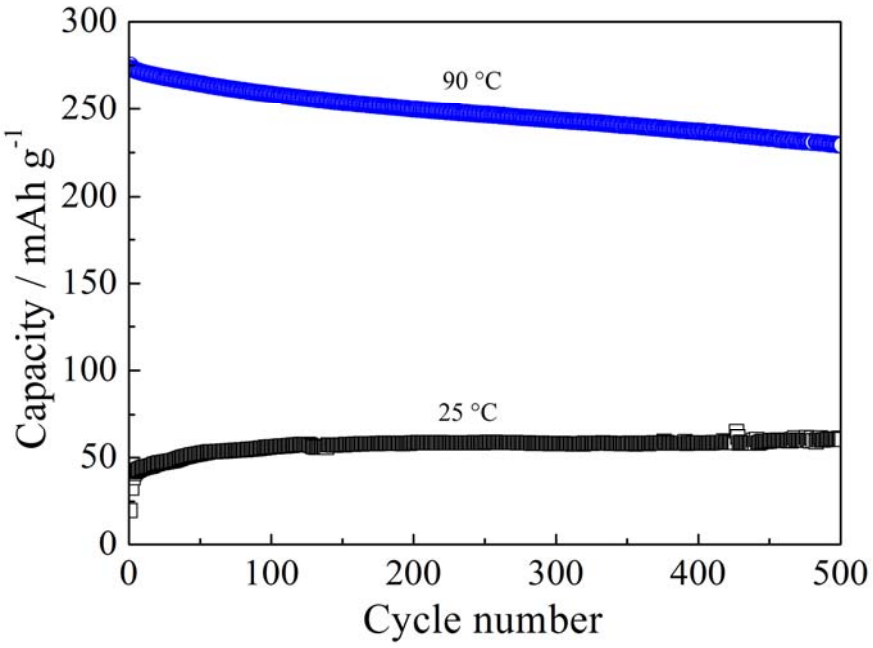

Fig. 5 Cycling performance of the HC electrode at 25 and 90 ºC. Current rate: 200 mA $(g\text{-}HC)^{-1}$.

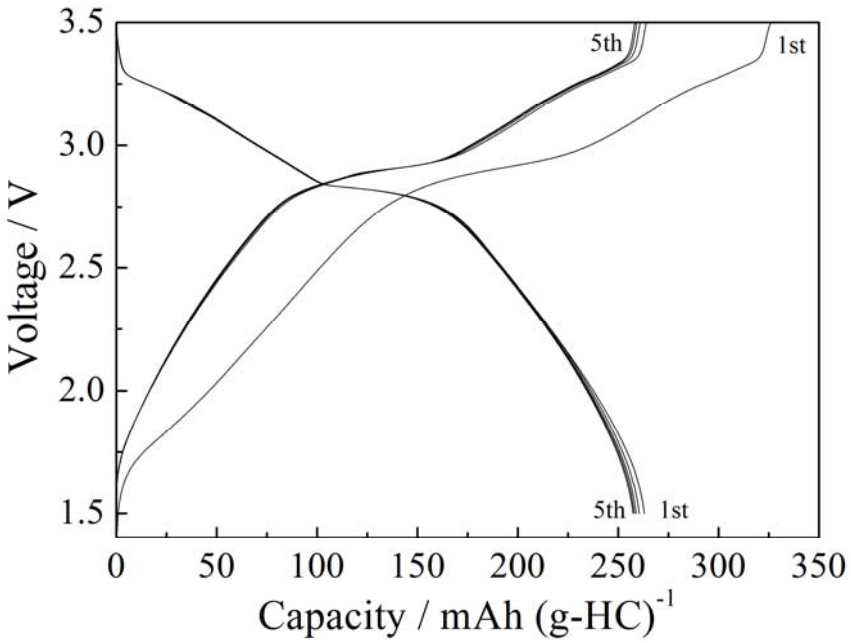

Fig. 6 Charge-discharge curves of the HC/$NaCrO_2$ full cell at 90 ºC with a current rate of 20 mA $(g\text{-}HC)^{-1}$.